

# Structural, photoconductivity and electro-luminescence studies of Mn doped Barium Tartrate crystals

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Conditions for the growth of crystals of Mn doped Barium Tartrate (BaTr) by controlled ionic diffusion of reactants through silica hydrogel have been optimized. The confirmation of the crystal formation was done by carrying out Powder XRD and TGA. Here the authors made an attempt to explore the photo-electronic properties of the prepared crystal and noticed that they are very much influenced by the presence of defects in the original crystal lattice. Photoconductivity (PC) studies of the material as a function of time, intensity of irradiation light, annealing temperature; applied voltage and concentration of the dopant (Mn) are studied. Electro luminescence (EL) of BaTr crystals are measured with the help of a photomultiplier tube (PMT) and its EL brightness is measured as a function of voltage of excitation at different annealing temperature and concentration of Mn. The imperfections in the crystal lattice some times act as traps or as recombination centers. Luminescent centers forms at the cracks, voids, dislocations and stacking faults. These defects provide sites for the precipitation of the excess carriers if it is produced.

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## 1. Introduction

Most of the tartrate compounds are insoluble in water and decomposes before melting. Hence crystals of such type of compounds cannot be grown by either slow evaporation or melt techniques. In this situation gel method is the appropriate one for the growth of BaTr crystals. Crystal growth in gels offers itself as a simple and inexpensive method for useful experiments on the growth of tartrate crystal. Surveys of growth in gels have been made by Henisch [1] and Arora [2]. Compounds of tartaric acid find several practical applications in Science and Technology [3]. Tartrate single crystals show many interesting physical properties such as ferroelectric, piezoelectric, dielectric, optical and other pertinent characteristics. They are used for non-linear optical devices based on their optical Second Harmonic Generation, optical transmission characteristics, fabrication of crystal oscillators and resonators and controlled laser emission [4-9].

Barium Tartrate (BaTr) is a quite interesting compound and hence some attempts have been made to grow its Mn doped crystals. Divalent manganese as a luminescent center has been of widespread interest both because of its presence in a large number of commercially important phosphors and because of its unusual properties. BaTr crystallizes in orthorhombic system in the space group  $P_{212121}$  ( $C_{2v}$ ) containing four molecules / unit cell. Its unit cell dimensions are  $a = 7.59 \text{ \AA}$ ,  $b = 23.78 \text{ \AA}$  and  $c = 7.536 \text{ \AA}$  (JCPDS – CAS: 66904-98-1). Thermal behaviour of gel grown tartrates of Yttrium & Samarium [10], mixed rare earth (Didymium) [11], Iron [12] and Strontium [13] was also reported. Strontium tartrate is

identified for pyroelectric and ferroelectric transitions [14].

Conversions of both light into electricity (solar cell) and electricity into light (EL) of various wave length throughout the UV-VIS-IR range in a quantum system can occur from the absorption or emission of a photon [15]. The electro-optical phenomena considered here are (i). Photo Conductivity (PC), which concerns with detection of optical signals through electronic processes and (ii). Electro Luminescence (EL), the conversion of electrical energy into optical energy.

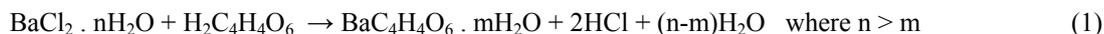
In this paper we are reporting the structural, photoconductivity and electro luminescence properties of BaTr crystals and the effect of Mn doping on these properties. We have chosen this gel method because of the ease of preparation of the sample by controlling preparative parameters.

## 2. Experimental

Crystals of BaTr have been grown by the gel method at room temperature. This technique consists of incorporating one reactant in the gelling mixture and then diffusing another reactant into the gel, leading to high super saturation and the initiation of nucleation and crystal growth [16]. The crystallization apparatus used were test tubes of 20 mm diameter and 20 cm length. AR grade chemicals were used to grow the crystals. The required quantity of distilled water is added with Sodium Meta Silicate to obtain a specific gravity of 1.04 gm/cc. Then 1M Tartaric acid solution was added to this solution to form a gel of pH value 5-6. It took about 24 hours for the

gel to set. Over the set gel an aqueous solution of 1M Barium chloride was gently poured down the walls of the

tube. The following reaction is expected to occur during the process.



Within two days the onset of crystallization could be discerned. The resulting gel-liquid interface is then kept at room temperature for a period of 2 to 3 weeks. During this time a number of good quality and large size BaTr crystals appeared in the gel medium and the crop is harvested. The number of crystals in the test tube depends on various factors like molarity, density, pH value and quantity of solution. Mn doped BaTr crystals were prepared by changing the concentration (from 0.5M to 5M) of AR grade  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (from CDH) in  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  solution.

Transparent Conducting Oxide (TCO) thin films are essential for the conduct of PC and EL experiments. We have prepared transparent conducting  $\text{SnO}_2$  films by a cost effective vapour deposition technique [17, 18]. PC and EL cells used for the present investigation were prepared by pressing the BaTr powder between the transparent conducting  $\text{SnO}_2$  films of resistance  $\sim 150 \Omega/\text{cm}^2$  and copper plate at a gap of 100  $\mu\text{m}$  for a given area.

### 3. Results and discussion

#### 3.1 Structural properties

The structure of the tartrate ion has been determined by many authors using X-ray diffraction [19–24]. The ion consists of two planar halves, each containing a carboxyl group, a tetrahedral carbon atom and hydroxyl oxygen atoms. The chain of carbon atoms is almost planar. The planes of two  $\text{CO}_2$  groups are inclined nearly at  $60^\circ$  to the plane. Hence  $C_{2v}$  symmetry is assumed for the tartrate ions. Structure of the BaTr crystals were studied by taking XRD using  $\text{Cu K}\alpha$  ( $\lambda = 0.154056 \text{ nm}$ ) radiation from Bruker, D8 Advance, Germany and were compared with JCPDS data card.

The XRD analysis shows crystalline nature of the barium tartrate crystals by the orientation along (013) plane (evidenced by the peak at  $2\theta = 36.192^\circ$ ). The presence of other orientations such as (040), (121), (131) and (230) was also detected at  $2\theta = 14.808^\circ$ ,  $18.287^\circ$ ,  $19.872^\circ$  and  $26.015^\circ$  respectively with lower intensities. On Mn doping few extra peaks were detected with lower intensities but the intensity of the prominent peak is decreased and that of certain other peaks were increased. On increasing the concentration of the dopant, the intensity of the prominent peak further decreased and others increased due to the decrease and increase in the atomic density of Mn in these planes respectively. The decrease in peak intensities is due to the replacement of  $\text{Ba}^{2+}$  ions with  $\text{Mn}^{2+}$  ions in the lattice of BaTr crystals. Increase in dopant concentration leads to the movement of  $\text{Mn}^{2+}$  ions to the interstitial sites and also increases the amorphous phase and disorders. The XRD pattern of BaTr crystals doped at different concentrations of Mn is given in Fig. 1.

#### 3.2 Thermal studies

The thermal decomposition behaviour was studied by Thermogravimetry (TG) by Perkin Elmer-Pyris Diamond – USA. Fig. 2 shows the TG curve recorded for BaTr crystals. The results are quite similar to those reported for tartrate [13, 25, 26] thereby reconfirming the BaTr crystal formation.

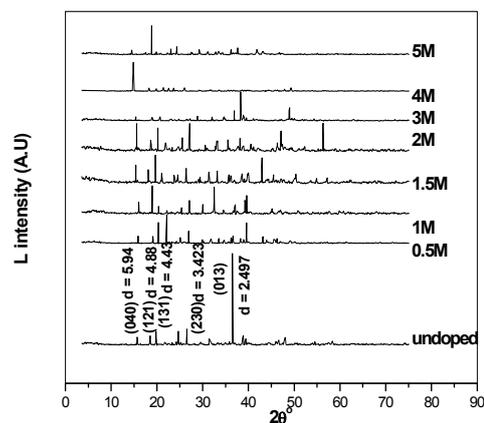


Fig. 1. XRD patterns of Mn doped BaTr crystals.

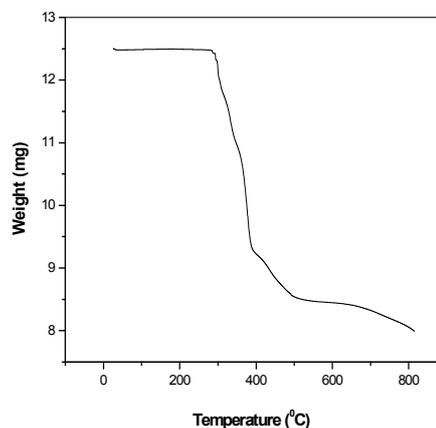


Fig 2. TG curve of BaTr crystals.

#### 3.3 Photo conductivity (PC)

It is the increase in the electrical conductivity of the material because of additional carriers created due to optical absorption. The important processes involved in PC are absorption, photo generation and recombination. The study of PC of semi conducting materials has gained

industrial importance owing to its use in PV devices [27].

PC studies of BaTr crystals were performed by using a 100W milky lamp as excitation source. The samples are annealed at various temperatures upto 200°C with the help of an electric furnace. The photocurrent was recorded by a digital nano-ammeter, model DNM-121 (Scientific equipment, Roorkee, India ).

Photo-electronic properties of the prepared crystals are very much influenced by the presence of defects in the original crystal lattice. The imperfections in the crystal lattice some times act as traps or as recombination centers. PC increases as annealing temperature increases and becomes maximum at 100°C and then decreases Fig. 3. The main purpose of annealing is to increase the crystallinity of the BaTr crystals which produces an increment in photocurrent. Increase in photo current with temperature up to 100°C can be explained also on the basis of impurity effect in the material. Imperfections acting as efficient recombination centers decrease the photosensitivity. Also imperfections having high probability for capturing the minority carriers with subsequent small probability for capturing a majority carrier increase the photosensitivity. The decrease in PC beyond 100°C is due to the increase in the amorphous phase and disorders and also due to the recombination of electrons which are thermally freed from traps with photo excited holes held at centers as in quenching effects reported [28].

A representative plot of the time dependence of the photocurrent (primary photocurrent) of the sample at 100°C is shown in Fig. 4. It is found that maximum value of photocurrent increases with increasing intensity of excitation Fig. 5 and also with increase in applied voltage (Fig. 6). Along with the increase in intensity and applied voltage more and more charge carriers reach at the respective electrodes and the photocurrent increases. The non-linearity in Figs. 5 and 6 represents the dependence of maximum value of photocurrent (secondary photocurrent) on the intensity of excitation and applied voltage. The variation in photo current can be expressed in terms of a two centre model. According to this model when the hole demarcation level is lowered through the level of sensitizing centres by increasing the light intensity at a constant temperature, the photo sensitivity increases as the electron life time increases, giving rise to super-linear or sub-linear photo conductivity. Fig. 7 shows the variation of the maximum value of photocurrent with concentration of the dopant. As the concentration increases the charge carriers also increases and it is observed that PC increases and reaches maximum at 1.5 M concentration of Mn. At this concentration the charge concentration seems to be optimum for better PC. As the concentration of Mn increased PC is found to be decreased because of the chance of more carrier collision probability during charge transport due to concentration quenching.

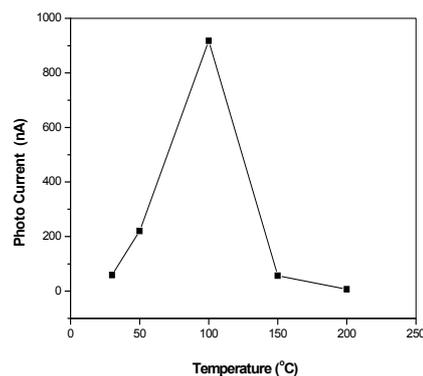


Fig. 3. PC of BaTr crystals with temperature.

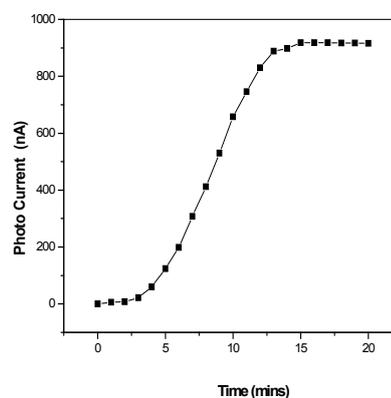


Fig. 4. PC of BaTr crystals with respect to time.

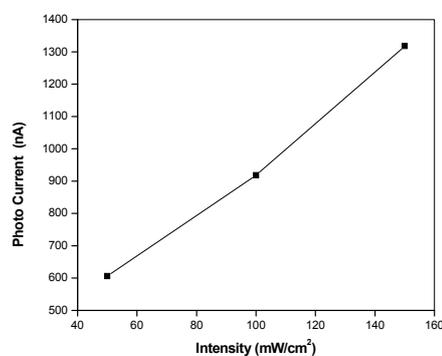


Fig. 5. PC of BaTr crystals with intensity of light.

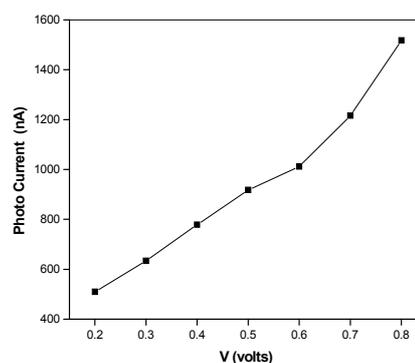


Fig. 6. PC of BaTr crystals with applied voltage.

### 3.4 Electro-luminescence (EL)

EL is the phenomenon of the emission of e-m radiation from condensed matter subjected to an external electric field. The observation of EL was first reported by Round [29] of the Marconi company when working with SiC crystals for the detection of radio waves. But the phenomenon was originally discovered by Lossev [30–32]. This effect in inorganic phosphors was first observed by Destriau [33–35]. Organic EL observed for the first time by Bermanose and co-workers [36, 37] has long been of interest from a basic research point of view because of the insights that can be gleaned regarding the electronic processes in solids bonded by weak Van der Waals interactions [38]. There is a growing interest in organic EL. A great deal of progress has been made recently in improving the performances of various classes of organic EL devices.

The experimental ac/dc powder EL cells used for the present investigation is essentially a parallel plate condenser with the BaTr powder between the transparent conducting SnO<sub>2</sub> films and copper plate with no binder for enhancing the dielectric strength. The EL brightness as a function of applied a.c. & d.c voltage (0–1500 V ac/dc power supply) was measured with a photomultiplier tube (PMT) (RCA 931A). The light emitted from the EL cell on application of suitable voltage was detected by the PMT and the corresponding photocurrent is measured with the help of a digital nanoammeter.

#### 3.4.1 AC Electro-luminescence

Luminescent centers formed at the cracks, voids, dislocations and stacking faults provide sites for the precipitation of the excess carriers if it is produced. Electrons and holes are injected into the host material from both the electrodes and also from the defects on the application of the field. The electrons from the donor centers or from the intrinsic electron traps are freed by the electric field and they enter the conduction band, where they are accelerated by the positive half cycle of the field until they gain sufficient kinetic energy to ionize or excite activator centers by the elastic impact. In the reverse half cycle of the field these electrons recombine with the luminescence centers with emission of characteristic radiation. This mechanism corresponds to the impact ionization of the activator centers [35, 39–41]. If the next pulse is of the same polarity as the preceding one, the system is already partially polarized, so that the light output is necessarily reduced, since not only is the internal electric field lower, but there are now fewer electrons trapped at the defects. The justification for this argument is that light was observed to be emitted locally in the form of comet. The light from a single appears in double comet lines, each half of which lights up alternately, as the field

is reversed and the nearer electrode turns positive. The integrated light intensity of large number of comets of different length is accurately given by the expression [39, 42–44]

$$B = A \exp(-C/V^{1/2}) \quad (2)$$

over many orders of magnitude of luminance. Where A and C are constants independent of the voltage. The constant A more or less describes the source of charge carriers responsible for the excitation process while C is a complex quantity which relates to the local field intensity. This relationship follows the normal law over many decades of EL brightness.

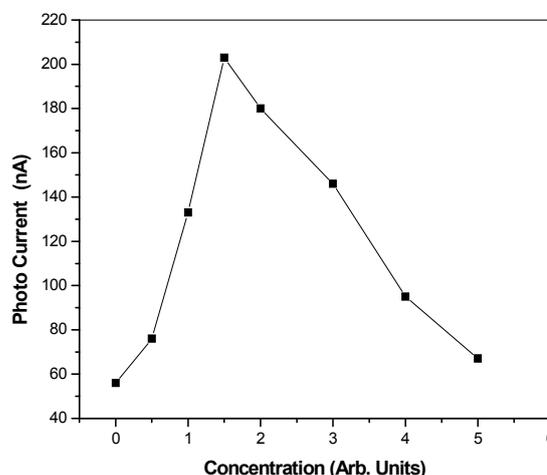


Fig. 7. PC of BaTr crystals at different concentrations of the dopant (Mn).

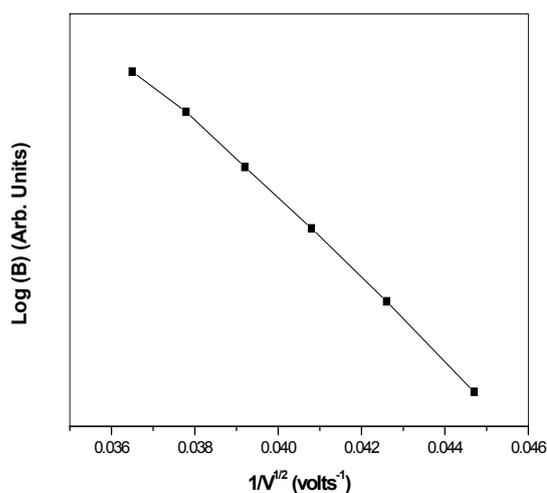


Fig. 8. Plot of  $\text{Log}(B)$  Vs.  $V^{-1/2}$ .

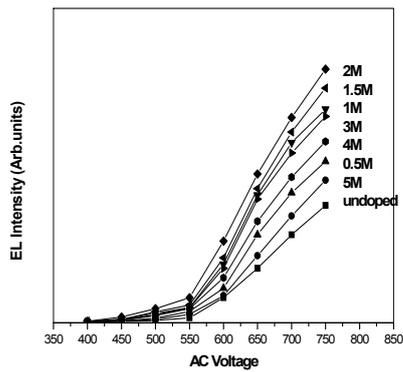


Fig. 9. AC EL of BaTr crystals at different concentrations of the dopant (Mn).

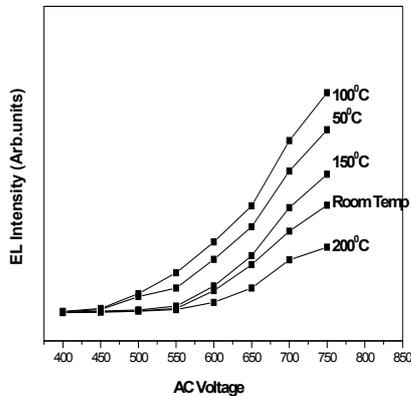


Fig. 10. AC EL of BaTr crystals at different annealing temperature.

This expresses that the mechanism of excitation is acceleration- collision one. Log (B) [Brightness] versus  $V^{-1/2}$  (applied a.c voltage), of BaTr electroluminor is given in Fig. 8. Linearity of the plots holds the above relation. AC EL Brightness as a function of applied a.c voltage of BaTr electroluminor at different concentrations of the dopant (Mn) is given in Fig. 9. EL intensity increases with increasing Mn concentration and reaches maximum at 2 M then decreases on increasing concentration due to concentration quenching. AC EL intensity of BaTr electroluminor at different annealing temperatures are given in Fig. 10. EL intensity increases with increasing annealing temperature (crystallinity increases) and reaches maximum at 100°C then decreases on increasing annealing temperature due to the increase in the amorphous phase and disorders. The overall AC EL emission of BaTr electroluminor is bluish one because the intensities of longer wavelengths are poor if they are present.

### 3.4.2 DC Electro-luminescence

DCEL powder panels have become reasonably successful as displays. An efficient DC powder EL device

was first reported by A. Vecht [45]. Two essential features of any DC EL panel are that the phosphor particles are in contact with each other and with the electrodes. On the initial application of a DC voltage, a high current flows and no light is observed. This is because the high conductivity of the phosphor surface and the inter particle contacts precludes any current flow through the particles themselves. At a critical power density the current falls and light emission appears at the positive electrode. An increase in applied voltage produces a temporary rise in current density but this falls rapidly and the panel brightness increases. This is termed as forming process. To form the device a ramped d.c voltage is applied with the copper electrode negative. At first the current increases with increasing voltage and no light is emitted, until the current begins to decrease at a particular voltage when the emission of visible light begins. This initial phase of forming is accompanied by a reduction in current by 3 to 100 times depending on the pre-treatment of the powder. Continued increase of the voltage leads to a further increase in resistance of the panel. Practically all the applied voltage is then dropped across the formed region and EL emission is obtained from the formed layer.

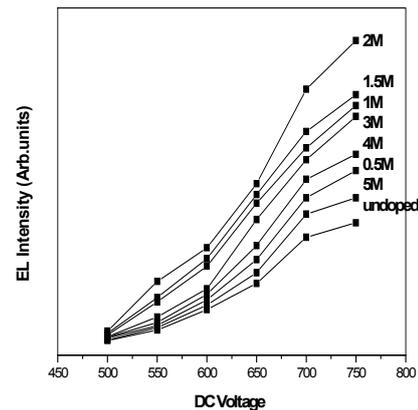


Fig. 11. DCEL of BaTr crystals at different concentrations of the dopant (Mn).

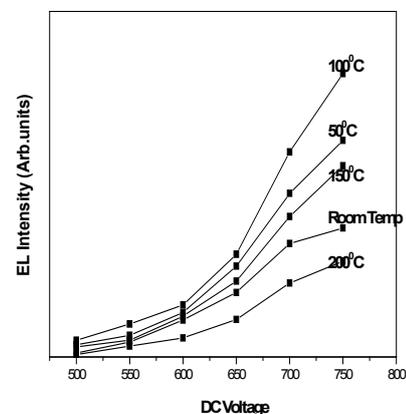


Fig. 12. DCEL of BaTr crystals at different annealing temperature.

DC EL Brightness as a function of applied d.c voltage of BaTr electroluminor at different concentrations of the dopant (Mn) is given in Fig. 11. EL intensity increases with increasing Mn concentration and reaches maximum at 2 M then decreases on increasing concentration due to concentration quenching. DC EL intensities of BaTr electroluminor at different annealing temperatures are given in Fig. 12. EL intensity increases with increasing annealing temperature (crystallinity increases) and reaches maximum at 100°C then decreases on increasing annealing temperature due to the increase in the amorphous phase and disorders. The overall DC EL emission of BaTr electroluminor is bluish one because the intensities of longer wave length are poor if they are present.

#### 4. Conclusions

In this paper we have attempted to present the electro-optical properties of the barium tetratrate crystals grown by the gel method at room temperature. The XRD analysis shows crystalline nature of the barium tetratrate crystals along (013) plane at  $2\theta = 36.192^\circ$ . The presence of other orientations such as (040), (121), (131) and (230) was also detected at  $2\theta = 14.808^\circ$ ,  $18.287^\circ$ ,  $19.872^\circ$  and  $26.015^\circ$  respectively with lower intensities. On Mn doping few extra peaks were detected with lower intensities but the intensity of the prominent peak is decreased and certain other peaks were increased. The results of TG studies are quite similar to those reported for tartrates.

PC effects of the crystals were studied and found that the material is more photosensitive at 100°C. The main purpose of annealing is to increase the crystallinity of the BaTr crystals which produces an increment in photocurrent. Increase in photo current with temperature up to 100°C can be explained also on the basis of impurity effect in the material. Imperfections acting as efficient recombination centers decrease the photosensitivity. Also imperfections having high probability for capturing the minority carriers with subsequent small probability for capturing a majority carrier increase the photosensitivity. The decrease in PC beyond 100°C is due to the increase in the amorphous phase and disorders and also due to the recombination of electrons which are thermally freed from traps with photo excited holes held at centers as in quenching effects reported.

It is found that maximum value of photocurrent increases with increasing intensity of excitation and also with increase in applied voltage. With the increase in intensity and applied voltage more and more charge carriers reach at the respective electrodes and the photocurrent increases. Mn doping makes the photosensitive BaTr more sensitive as well as more efficient as a photoconductor. As the concentration increases the charge carriers also increases and it is observed that PC increases and reaches maximum at 1.5M concentration of Mn.

Electro-luminescence brightness increases with the applied electric field. ac/ dc EL Brightness as a function of applied a.c/d.c voltage of BaTr crystals at different

concentrations of the dopant (Mn) shows that EL intensity increases with increasing Mn concentration and reaches maximum at 2 M then decreases on increasing concentration due to concentration quenching. ac/ dc EL Brightness as a function of applied a.c/d.c voltage of BaTr electroluminor at different annealing temperatures shows that EL intensity increases with increasing annealing temperature and reaches maximum at 100°C then decreases on increasing annealing temperature. Log (B) versus  $V^{-1/2}$  plot of BaTr electroluminor shows that the mechanism of excitation is acceleration- collision one. We were not able to record the EL spectra because of the low brightness intensity. The overall emission of BaTr electroluminor is bluish one because the intensities of longer wavelengths are poor if they are present. A disadvantage of PC /EL measurement is the need for good electrical contacts. One of the major problems in powder EL devices is the higher driving voltage which causes sparks thereby spoiling the EL cell. EL is very old and well advanced subject, but it still requires further improvement to enable one to use it for practical applications as powder EL devices.

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